The Importance of Quadrupolar Interactions in Determining the Structure of Solid Hydrocarbon–Fluorocarbon Compounds

By Norman M. D. Brown and Findlay L. Swinton*

(School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland)

Summary   Calculations of the contributions of quadrupole–quadrupole interactions to the intermolecular potentials of the molecular pairs benzene–benzene, hexafluorobenzene–hexafluorobenzene, and benzene–hexafluorobenzene have shown that, in complete agreement with X-ray structural data, the preferred orientation in the two pure solids is that in which neighbouring molecules are perpendicularly oriented whereas the molecules in the solid mixture are predicted to adopt a parallel, face-to-face configuration.

The majority of binary mixtures composed of benzene and related aromatic molecules with hexafluorobenzene form solid 1:1 compounds with melting temperatures greater than the melting temperatures of both pure components and this fact, together with all the thermodynamic measure-

ments relating to these mixtures in the liquid state, imply the presence of unusually strong fluorocarbon–hydrocarbon interactions.[1,2] This behaviour is in direct contrast to mixtures of aliphatic or alicyclic fluorocarbons with hydrocarbons. There is, to date, a complete lack of conventional spectroscopic evidence for charge-transfer forces in the aromatic fluorocarbon–aromatic hydrocarbon mixtures and the strong unlike interactions have been attributed to various electrostatic forces. No quantitative estimates have been made regarding these various possible electrostatic interactions owing to the lack of an experimental value for the molecular quadrupole moment of hexafluorobenzene. Recently Gierke, Tigelaar, and Flygare[3] have computed the molecular quadrupole moment of hexafluorobenzene by a method which gives for other, similar, molecules good agreement with experiment. The quadrupole tensor components for hexafluorobenzene are of *opposite* sign to those of benzene. The theoretical values derived by Gierke *et al*, expressed in S.I. notation, are

$$(Q_{zz})(C_6F_6) \equiv Q_1 = + 5 \cdot 74 \times 10^{-39} \text{ C m}^2,$$

$$(Q_{zz})(C_6H_6) \equiv Q_2 = - 2 \cdot 20 \times 10^{-39} \text{ C m}^2.$$

The potential, $u(r)$, between two quadrupoles situated a distance r apart is given by the expression[4]

$$u(r) = 3Q_1Q_2(1 - 5 \cos^2\theta_1 - 5 \cos^2\theta_2 + 17 \cos^2\theta_1 \cos^2\theta_2 +$$

$$2 \sin^2\theta_1 \sin^2\theta_2\cos^2\phi + 16 \sin\theta_1\sin\theta_2\cos\theta_1\cos\theta_2\cos\phi)/16\pi\epsilon_0 r^5$$

where θ_1 and θ_2 are the angles the individual molecules make with the radius vector joining their centres and ϕ is the angle of mutual orientation of the two quadrupole molecules. ϵ_0 is the permittivity of free space. When the two molecules are symmetrically situated

(a) face-to-face, $\theta_1 = \theta_2 = \pi/2, \phi = 0$,
(b) edge-to-edge, $\theta_1 = \pi, \theta_2 = 0, \phi = 0$, and
(c) mutually perpendicular to one another, $\theta_1 = \pi/2, \theta_2 = 0, \phi = 0$,

the above expression reduces to

(a) $u = 9Q_1Q_2/16\pi\epsilon_0 r^5$,
(b) $u = 3Q_1Q_2/2\pi\epsilon_0 r^5$, and
(c) $u = -3Q_1Q_2/4\pi\epsilon_0 r^5$.

These simple expressions have been used to calculate the intermolecular potentials due solely to quadrupolar inter-

action shown in the Table. The values of r are calculated from the accepted van der Waals' radii of the atoms involved and are supported by recent X-ray structural data.[5] The above calculation ignores the contributions to the intermolecular potential of normal London dispersion forces and of second-order forces of the type quadrupole-induced dipole.

TABLE. Quadrupolar interaction potentials (r in nm, u in kJ mol^{-1})

	Face-to-face	Edge-to-edge	Mutually perpendicular
Benzene	r 0·34	r 0·74	r 0·54
	u +13·0	u +0·8	u −1·7
Hexafluoro-benzene	r 0·36	r 0·81	r 0·585
	u +66·2	u +3·1	u −7·8
Benzene hexafluoro-benzene	r 0·35	r 0·775	r 0·563
	u −29·3	u −1·5	u +3·6

The data shown in the Table lead to the prediction that, in the two pure solid substances, the preferred orientation is that in which neighbouring molecules are oriented in a perpendicular manner whereas in the equimolar solid, the molecules should be arranged in a face-to-face configuration in an alternating layer structure. This is exactly what is found experimentally from X-ray structural data.[5] Thus quadrupole-quadrupole interactions are probably the major factor dictating the structure of these solid phases and also the reason why the melting temperature of the equimolar mixture is some 19 K higher than the melting temperatures of the two pure components.

Information concerning molecular orientations in the liquid state can be obtained from light scattering studies. Schmidt[6] has measured the variation of the anisotropic Rayleigh ratio with temperature of both benzene and hexafluorobenzene and has shown that his results can be interpreted by assuming that, at low temperatures, there are a preponderance of perpendicularly oriented molecules. Recent light scattering measurements on hexafluorobenzene–benzene mixtures[7] show that, as in the solids, the opposite molecular orientation is dominant with parallel orientations being favoured at temperatures just above the crystal melting temperature.

[1] D. V. Fenby, *Rev. Pure Appl. Chem.*, 1972, **22**, 55.
[2] F. L. Swinton, to appear in 'Molecular Complexes,' Vol. II, ed, R. Foster, Paul Elek, London, 1974.
[3] T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, *J. Amer. Chem. Soc.*, 1972, **94**, 330.
[4] A. D. Buckingham, *Quart. Rev.*, 1959, **13**, 183.
[5] E. G. Cox, D. W. J. Cruikshank, and J. A. S. Smith, *Proc. Roy. Soc.*, 1958, **247**, 1; N. Boden, P. P. David, C. H. Stam, and G. A. Wesselink, *Mol. Phys.*, 1973, **25**, 81; T. Dahl, *Acta Chem. Scand.*, 1971, **25**, 1031; 1973, **27**, 995.
[6] R. L. Schmidt, *J. Colloid Interface Sci.*, 1968, **27**, 516.
[7] N. M. D. Brown, J. F. Maguire, and F. L. Swinton, unpublished measurements.